Carbon Capture using a Nitrogen-Selective Membrane Process

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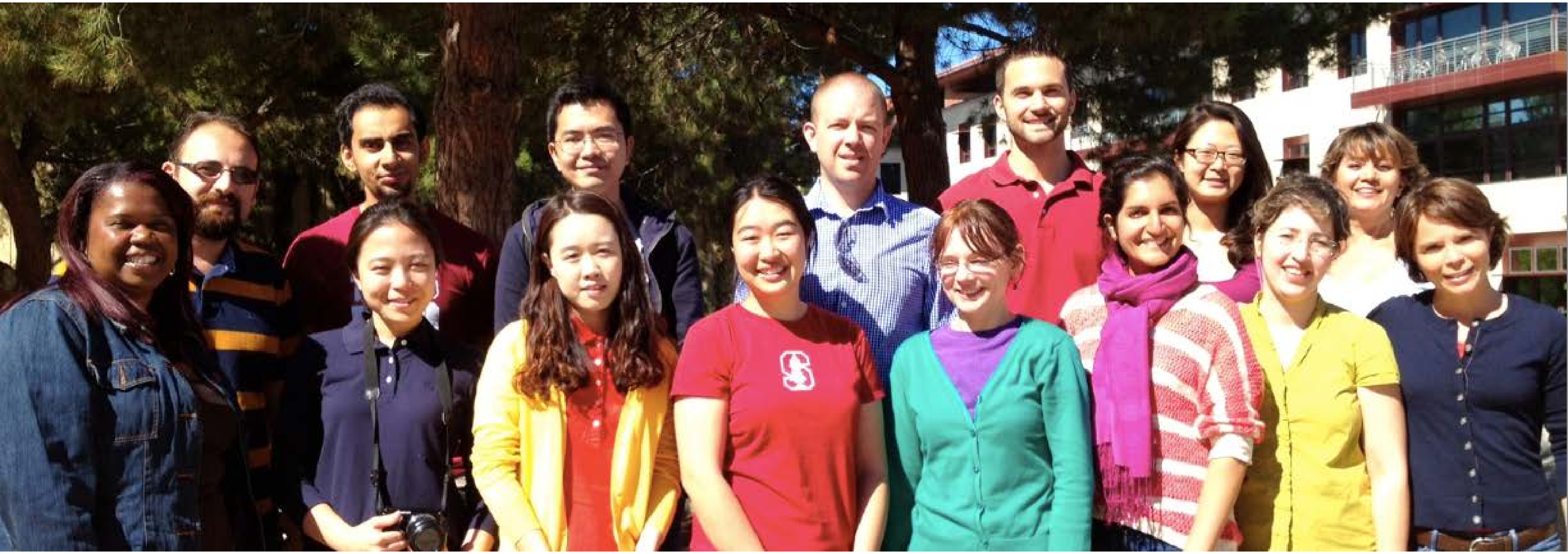
Clean Energy Conversions Team - 2014



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- Kyoungjin Lee (PhD)
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Clean Energy Conversions

Mission Statement: Tune and test materials for advanced energy conversion processes that minimize environmental impact

Ongoing Projects

1. Carbon Capture
   - N_2-selective membrane technology (EPA/NSF/ARL)
   - CO_2-selective adsorption (GCEP)
2. Carbon Sequestration
   - CO_2 transport and adsorption in micro/mesoporous systems, gas shale with kerogen and clay (DOE-NETL/BP/Aramco)
3. Trace Metal Capture
   - Hg, Se, As sorbent/catalyst testing (NSF/Johnson Matthey/EPRI/Novinda)
4. Hydrogen Fuel Cells and Storage
   - Oxygen reduction across Pt nanoparticles (Air Force/DOE)
   - Hydrogen production and storage (Shell/ARL/DOE)

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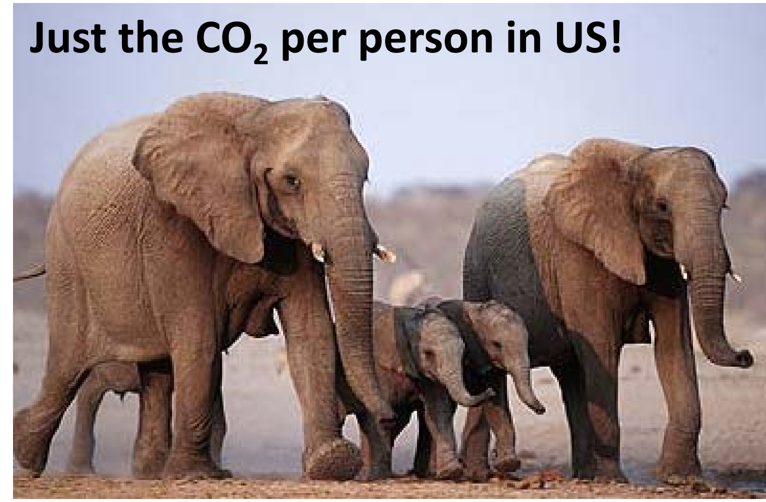
Agenda

Appreciating the Scale of CO_2 Emissions

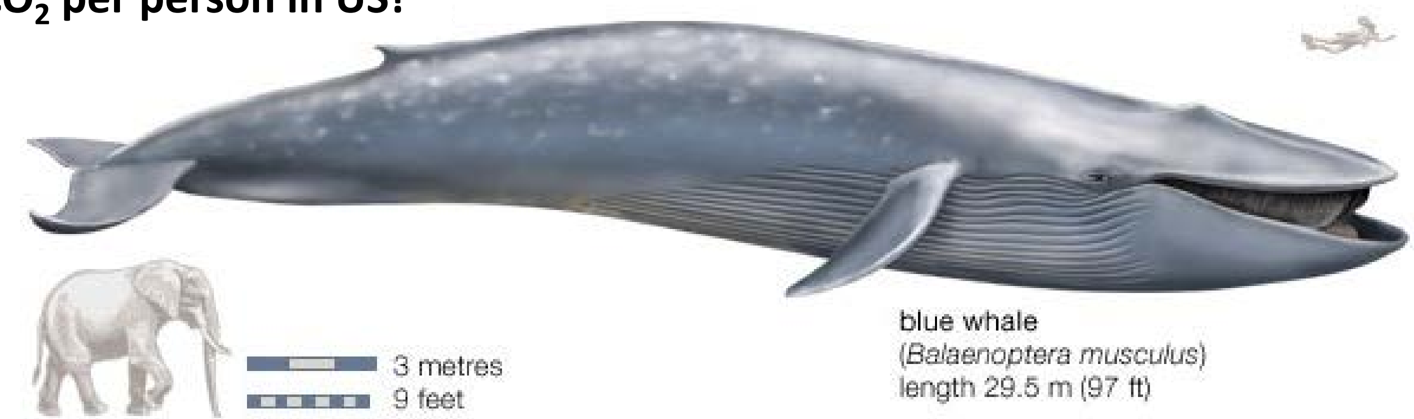
N_2-Selective Membranes

Appreciating the Scale

- US population ≈ 311,591,000
- CH population ≈ 1,344,130,000
- Annual emissions per capita:
  - US ≈ 17.5 tons CO_2
  - CH ≈ 5 tons CO_2
- Flight from SF to Chicago **RT** ≈ 0.8 ton CO_2
- Drive – Toyota Prius ≈ 0.7 tons CO_2
- Drive – BMW M3 convertible ≈ 1.5 tons CO_2
- Depending on sorbent loading and performance (cycling)
  - 17.5 tons ➔ total 150 tons material



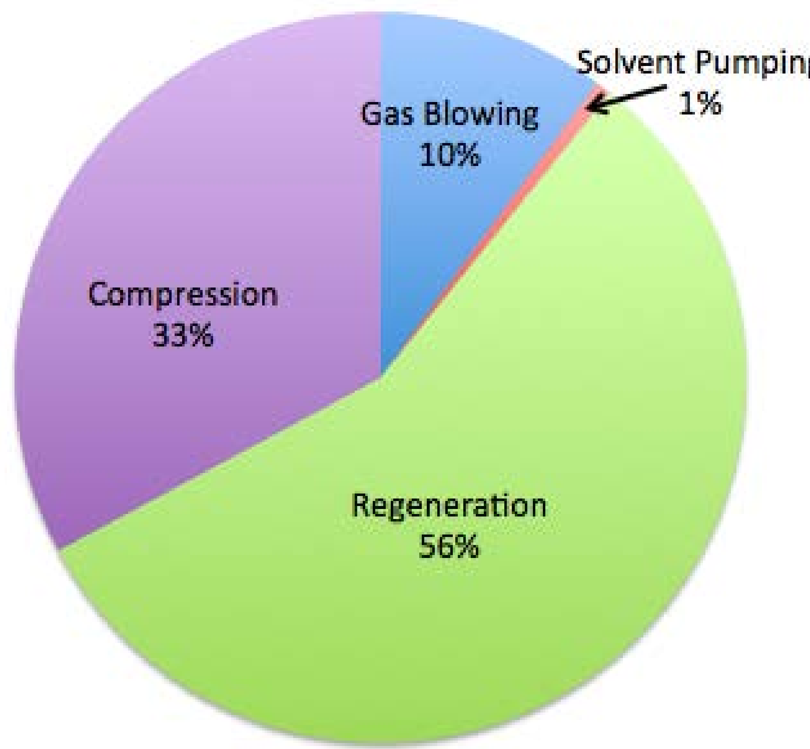
Just the sorbent + CO_2 per person in US!



Capture and Regeneration are Both Key

- Capturing CO_2 is only ½ the story
- MUST regenerate
- Options for usage:
  - Chemical feedstock?
    - Challenge – market is small
  - Enhanced oil recovery (aka EOR)
    - Seems to be best near-term option
  - Conversion to fuel
  - Storage
    - Challenges include public perception and overcoming risks of potential seismic events

Amine Scrubbing -
Current State-of-the-Art Technology for Point-Source Capture of CO_2



To Prevent 2 °C Warming …

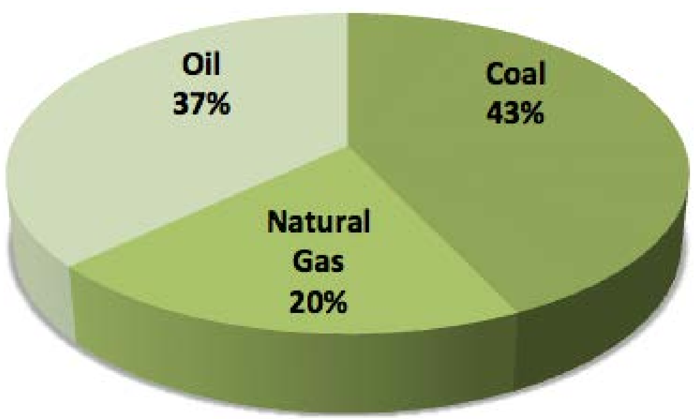
- Between 2000-2050 if cumulative emissions are less than:
  - 1,000 Gt → 25% probability global warming beyond 2 °C
  - 1,440 Gt → 50% probability global warming beyond 2 °C

Ref: Allen et al., Nature, 2009

Where we're projected to go (BAU):

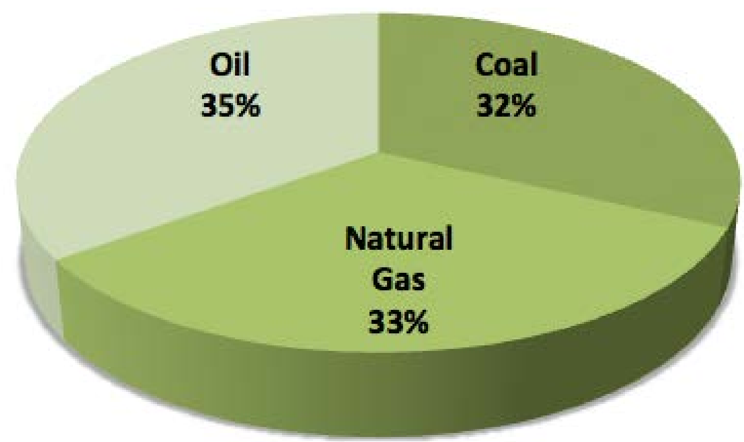
- Assuming annual increases:
  - Coal – 0.3%
  - Oil – 0.9%
  - Natural Gas – 2.3%
- ≈ 31 Gt CO_2 emitted in 2011
- ≈ 44 Gt CO_2 projected in 2050
- 1790 cum. Gt CO_2 in 2050!

Ref: BP Statistical Rev. of World Energy, 2012



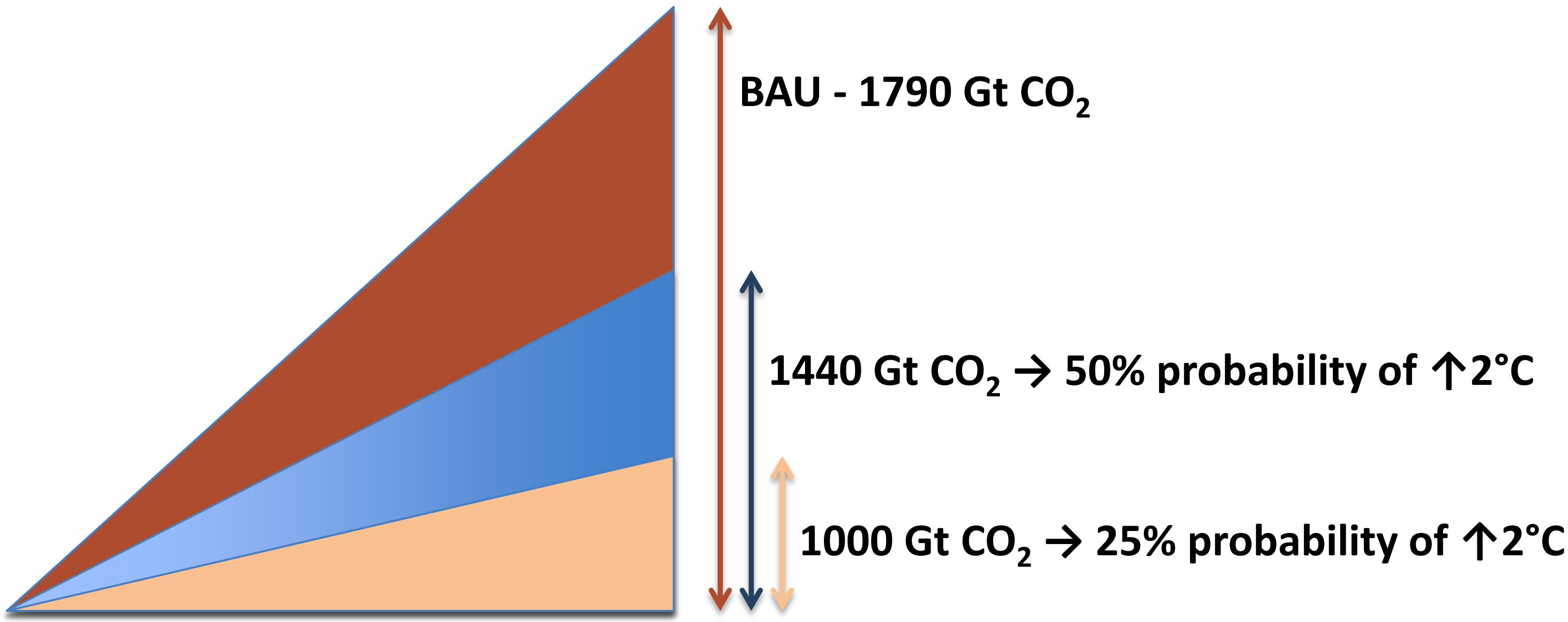
2009

BAU →



2050

Expanding the Impact of CCS



Scenario	Cumulative Gt CO_2
Replace Coal w/ NG	1512
90% Capture (Point Source Electric Sector)	1288
90% Capture (Point Source Electric Sector) + 50% Transport (on-board capture; EV; DAC)	1083

The Majority of the CO_2 Sources are Moderate to Extremely Dilute

Category	% CO_2 (vol)	Example	
High Pressure	varies	Gas Wells (e.g., Sleipner) Synthesis Gas (e.g., IGCC)	
High Purity	90-100%	Ethanol Plants Oxy-Combustion Exhaust	
Dilute to Moderate	10-20%	Coal-Fired Power Plants Cement Plants Cracker Exhaust	→ ~ 40% of emissions
Very Dilute	3-7%	Natural Gas Boilers Gas Turbines	→ ~ 20% of emissions
Extremely Dilute	0.04 – 1%	Ambient Air Submarines/ Space Craft	transport sector → ~ 25% of emissions

CCS Progress to Date

- 4 large-scale CCS projects have carried out monitoring sufficient to ensure injected CO_2 is permanently sequestered
- Combined, ~50 $MtCO_2$ has been stored
- 9 additional projects under construction + ~13 $MtCO_2$/yr and expected to be operational by 2016
- 2 possible demonstration projects at iron and steel plants and one at coal-to-chemicals/liquids – advanced stages of planning
- CO_2 pipeline transport is a mature technology w/ more than 3700 miles of pipelines in the U.S.
- CCS may be the primary large-scale option for emissions reductions from the industrial sector, e.g., cement, iron and steel, chemicals and refining, which represent ~20% of total global emissions
- CO_2 emissions from current systems under construction as of 2011 (e.g., power plants, industrial facilities, etc.) will total ~550 $GtCO_2$ through 2035

IEA CCS Roadmap, 2013; Global CCS Institute, 2013

Where CCS should be by 2050 - IEA

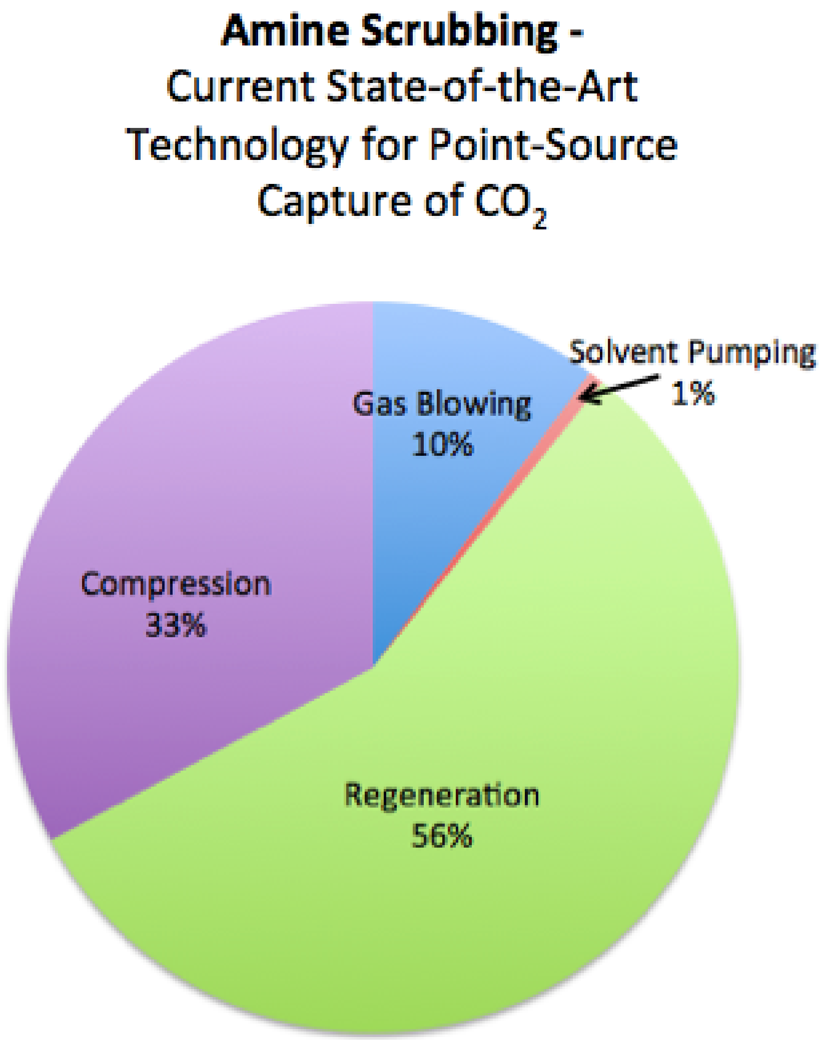
- IEA analysis shows that CCS is an integral part of any climate model where average global temperate increases are < 2-4 °C (Edmonds et al., 2010; IPCC, 2007)
- Growth needs to increase from tens of $MtCO_2$/yr → $GtCO_2$/yr from 2013 to 2050

Steps Required

- By **2020**, CO_2 capture must be successfully demonstrated in at least 30 projects across sectors - leading to over 50 $MtCO_2$/yr and safely and effectively stored
- By **2030**, CCS is routinely used to reduce emissions and is successfully demonstrated for industrial applications leading to over 2 $GtCO_2$/yr of storage
- By **2050**, CCS is routinely used to reduce emissions across power and industry sectors w/ over 7 $GtCO_2$ stored annually

IEA CCS Roadmap, 2013

Considering *other* Separation Process
Membranes and Adsorption

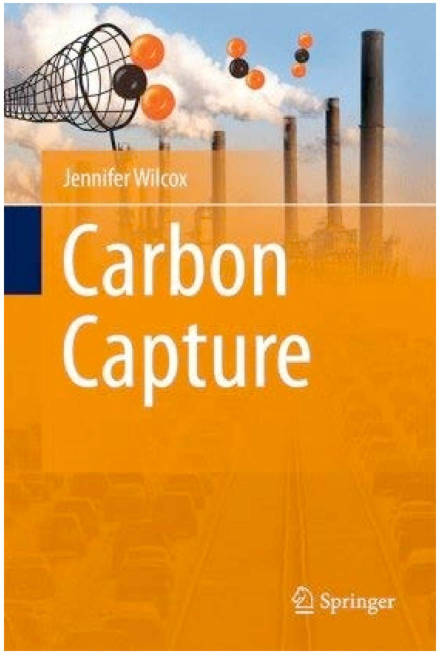


- Benefits of Adsorption:
  - Absence of water
  - Absence of corrosive solvents
  - Greater options for choosing heat properties
- Benefits of Membranes:
  - No regeneration
  - Space efficiency
  - No phase change

Wilcox et al., Annu. Rev. Chem. Biomol. Eng., to be published

… and finding ways not to bend CO_2

From Springer site:
http://www.springer.com/chemistry/book/978-1-4614-2214-3



Agenda

Appreciating the Scale of CO_2 Emissions

N_2-Selective Membranes

The Team - Theory, Experiments, and Optimization

Theory and Experiments



PhD students:
Ni Rochana, Ekin Ozdogan, Kyoungjin Lee

Optimization

PhD students:
Mengyao Yuan, Tao Narakornpijit

Post-doc:
Dr. Reza Haghpanah

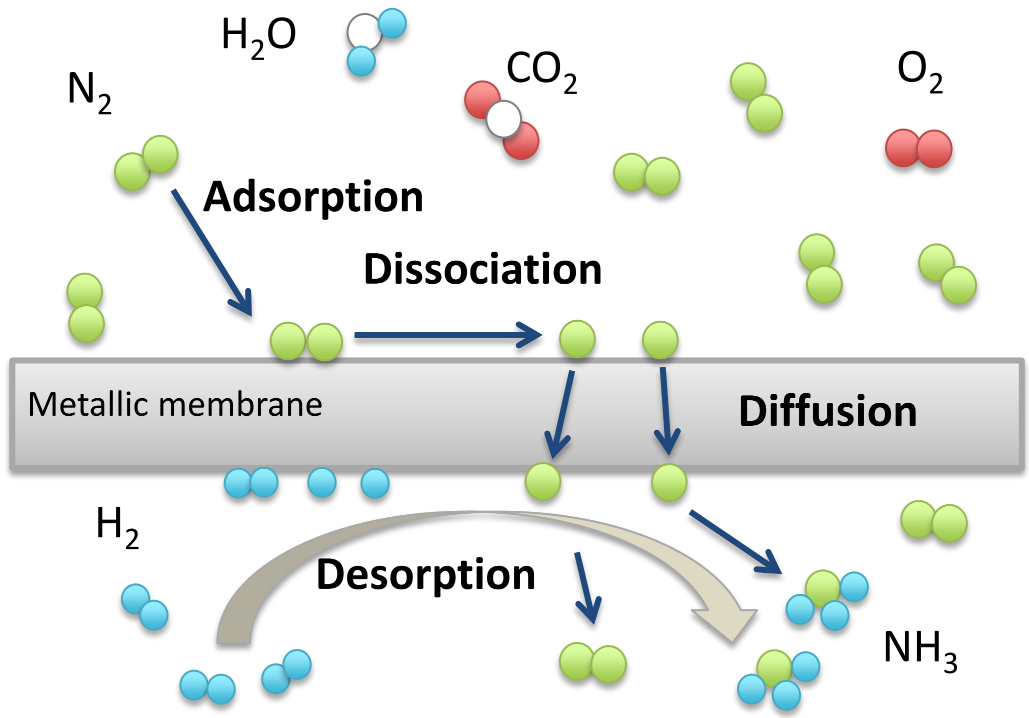


N_2-Selective Membrane for Carbon Capture

Flux:

$$J = \frac{Q}{L}\left(P^n_{feed} - P^n_{permeate}\right)$$

Q = Perm = Sol × Diff
L = Memb thickness



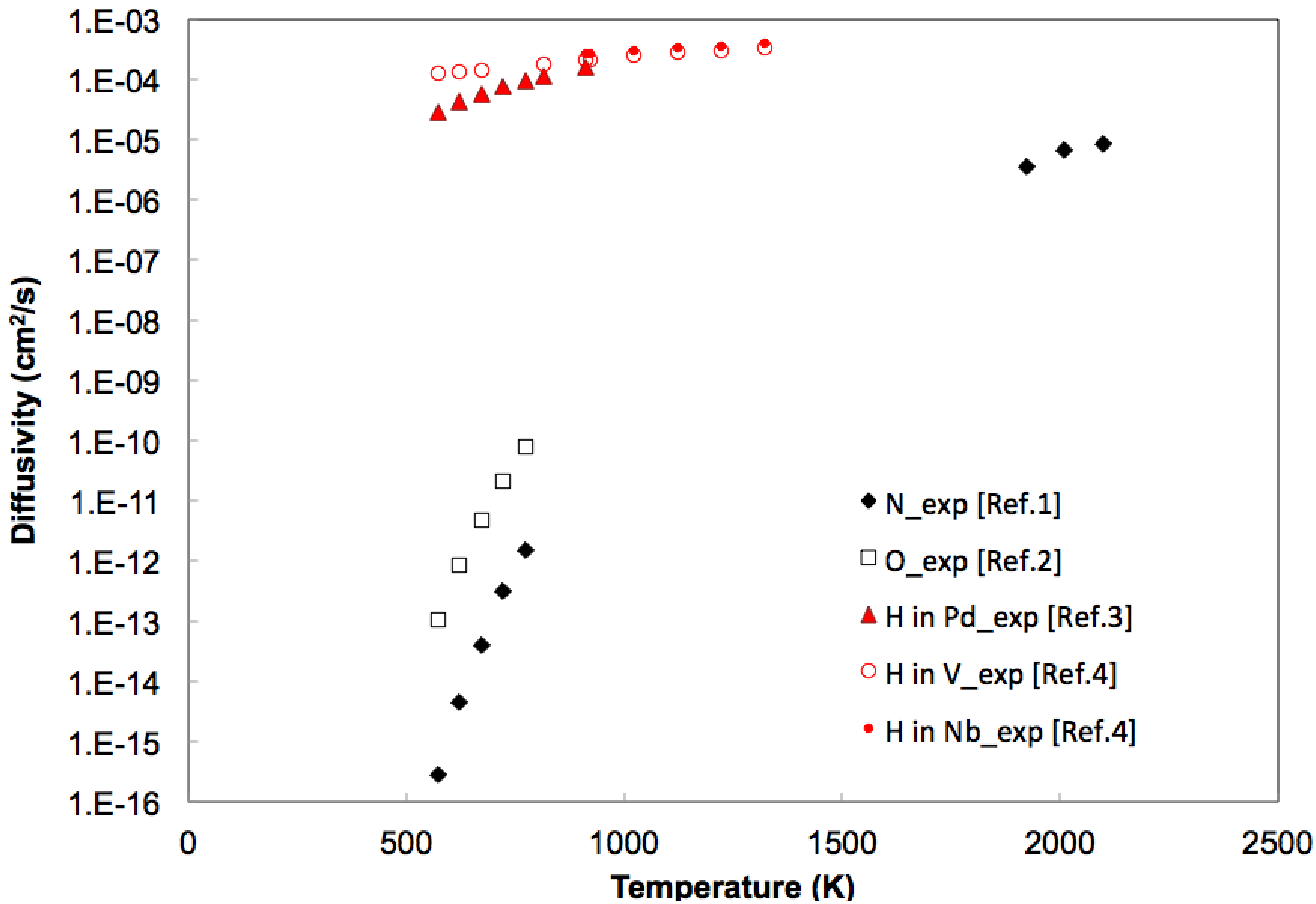
U.S. Patent 8,440,000

- Capture CO_2 on the high-pressure side of the membrane may lead to cost savings in terms of compression energy
- Separate solubility and diffusivity studies indicate N_2 can move through metals
- Potentially produce ammonia at lower energy costs

Rochana, Lee, Wilcox, J. Phys. Chem C, 2014

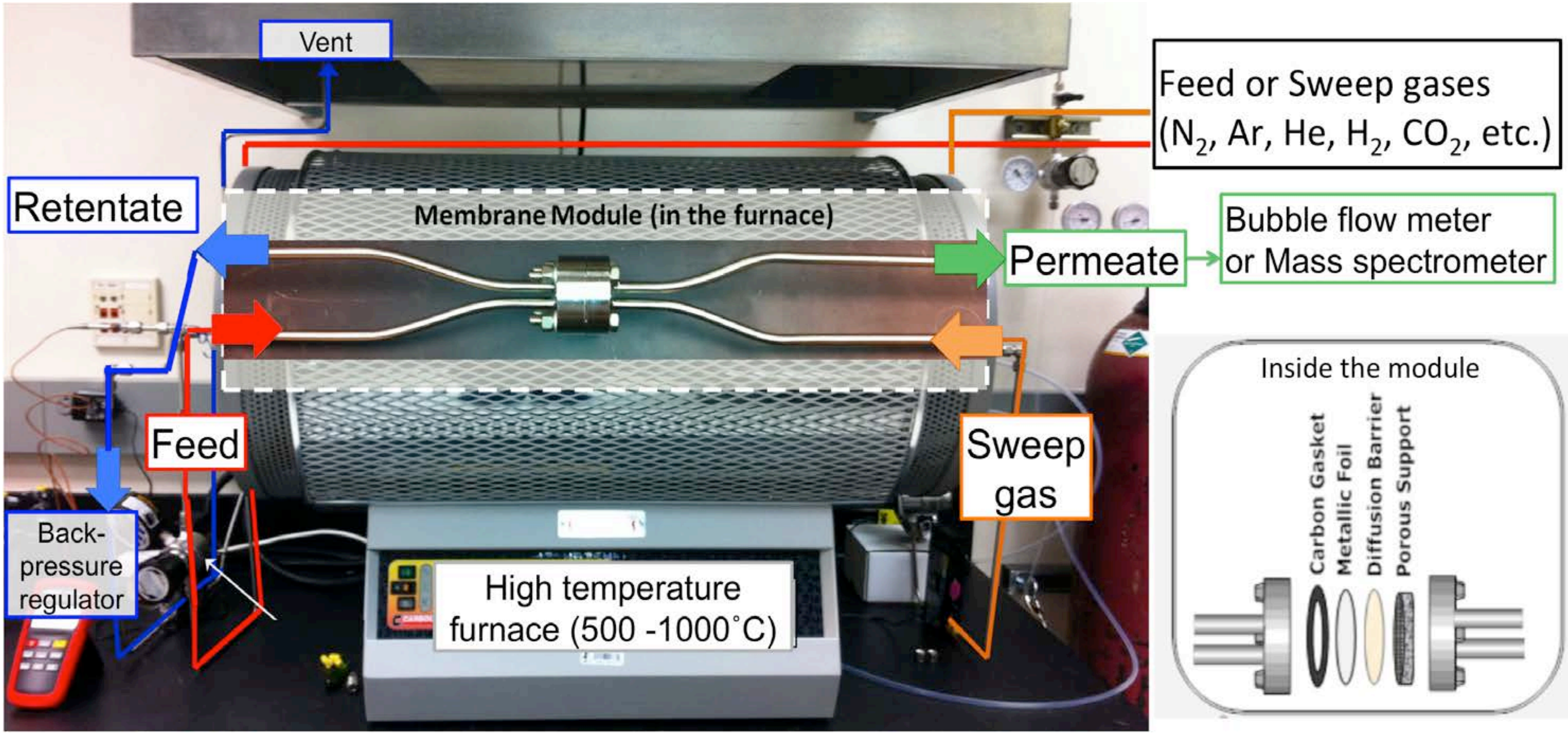
N and O Diffusivity in Vanadium

Permeability = Diffusivity × Solubility

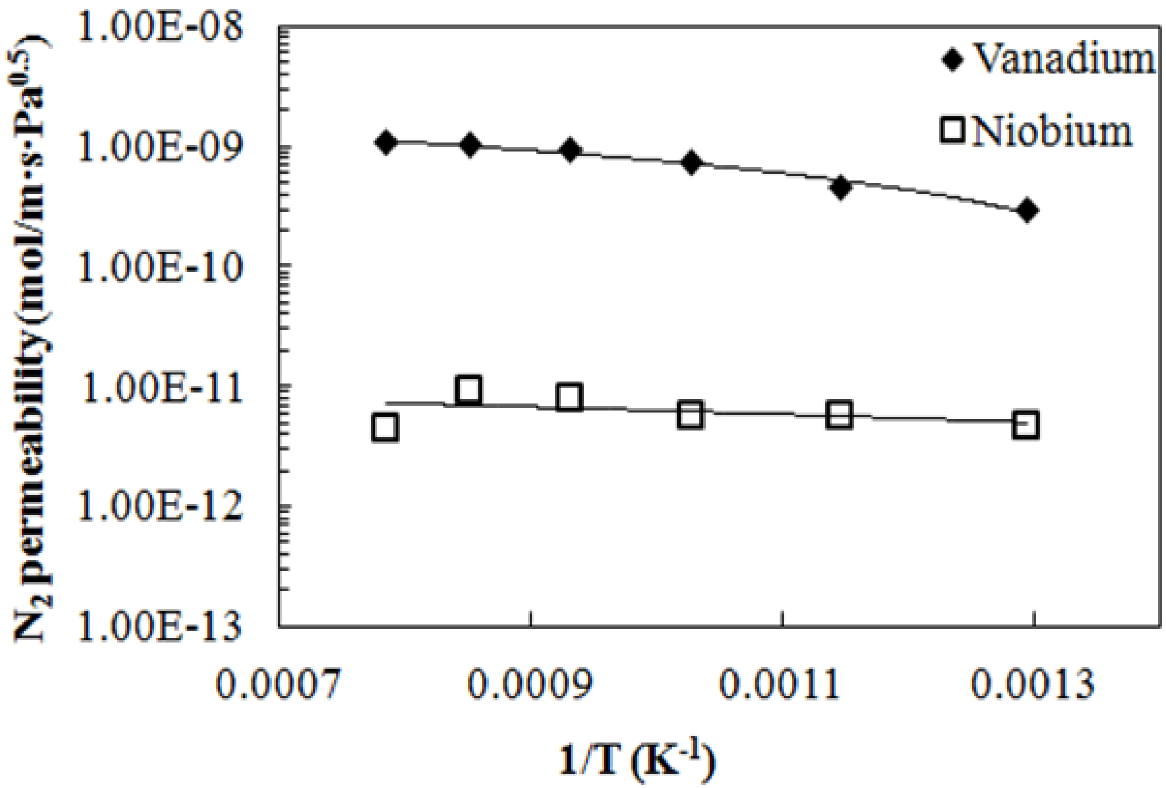


[1]Keinonen et al. *Appl. Phys.* A, 1984; [2]Nakajima et al. *Philosophical Magazine* A, 1993; [3]Holleck, *J. Phys. Chem.* 1970; [4] Fukai and Sugimoto, *Adv. In Phys.* 1985

Flux Measurements

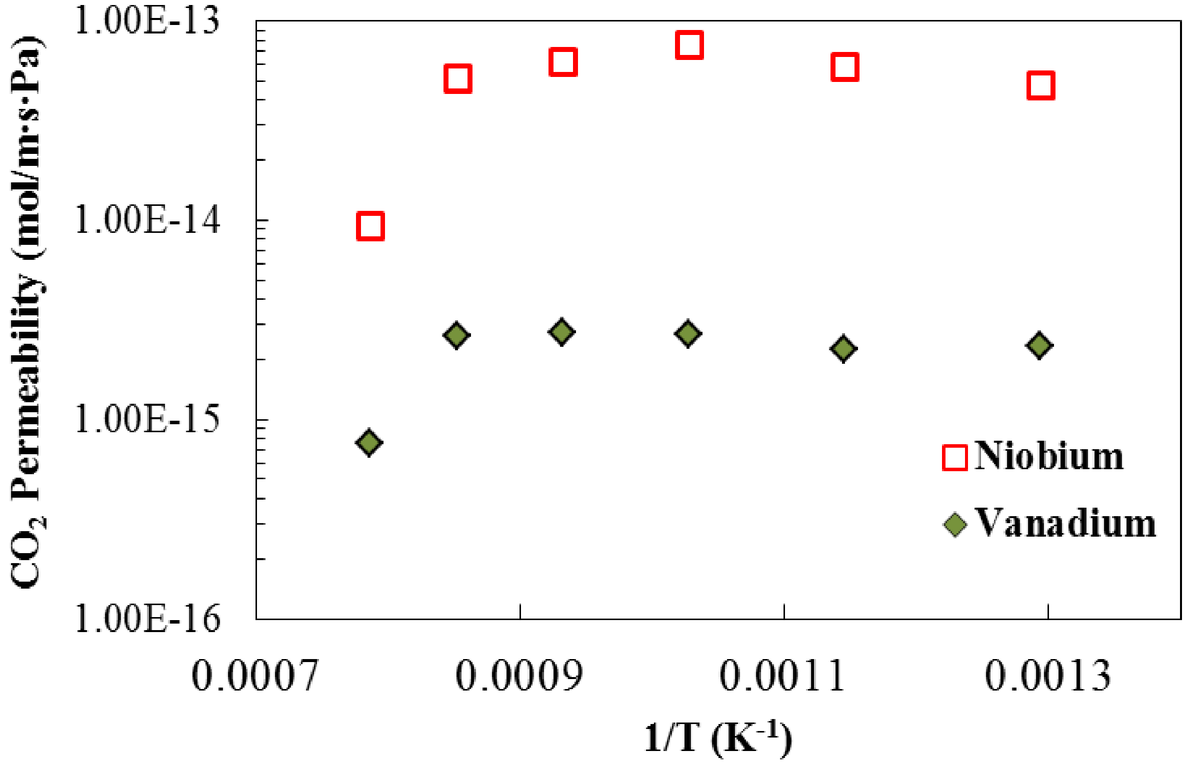


Nitrogen Permeability Measurement



- Nitrogen permeability through vanadium is higher by two orders of magnitude than its permeability through niobium
- Compare to the hydrogen permeability through Pd membrane (1.6×10^{-8} mole/m·s·$Pa^{0.5}$) – how can we increase this?

CO_2 Permeability Measurement

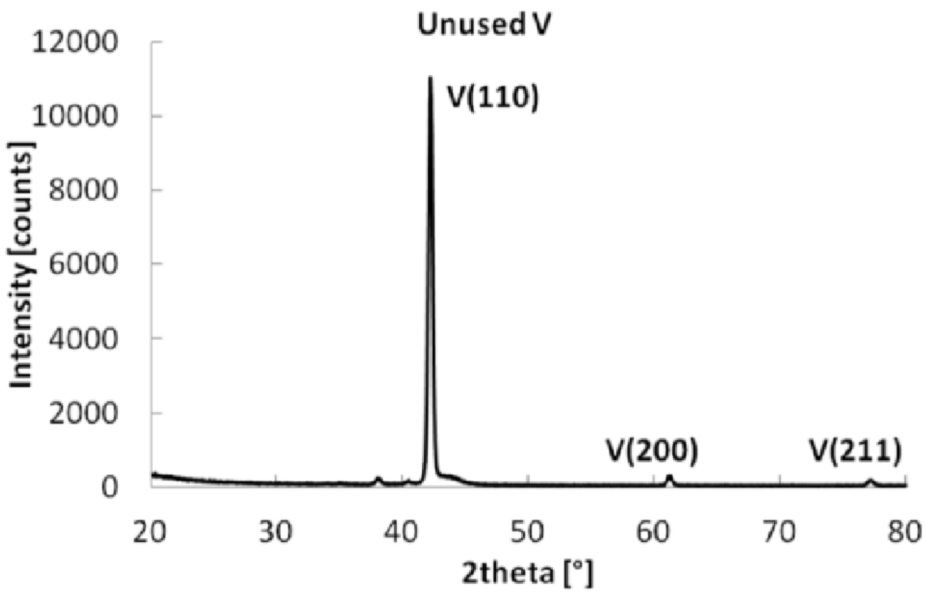


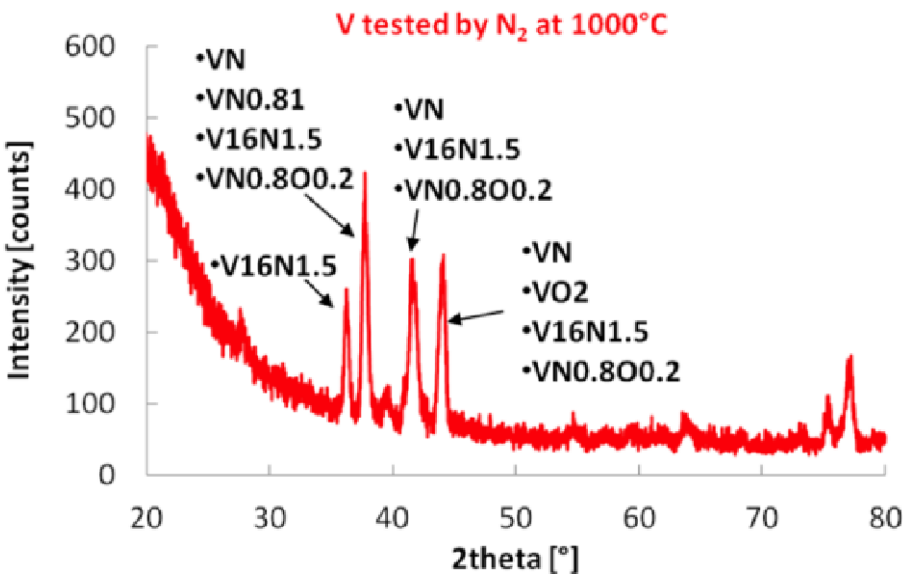
- CO_2 permeability is lower than nitrogen by <u>5 orders of magnitude</u> in vanadium
- CO_2 is expected to diffuse through the defects in the metals

Membrane *Bulk* After Permeation

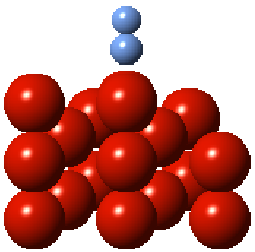
X-ray Diffraction (XRD) on V membranes

Bulk vanadium nitride phases formed after exposure to N_2 at high temperature



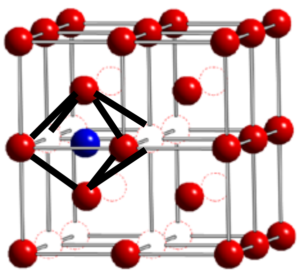


Material Screening and DFT



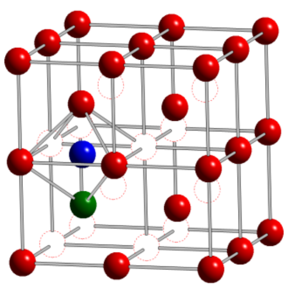
1. Surface activity

- N_2 adsorption mechanism
- N_2 dissociation pathway
- Comparison to other typical ammonia synthesis catalysts



2. Solubility and Diffusivity

- Atomic N binding mechanism
- Comparison to atomic H binding



3. Effect of alloying

- Ru
- Effect on binding
- Implications for permeability

Computational Methodology

VASP (Vienna *ab initio* Simulation Package)

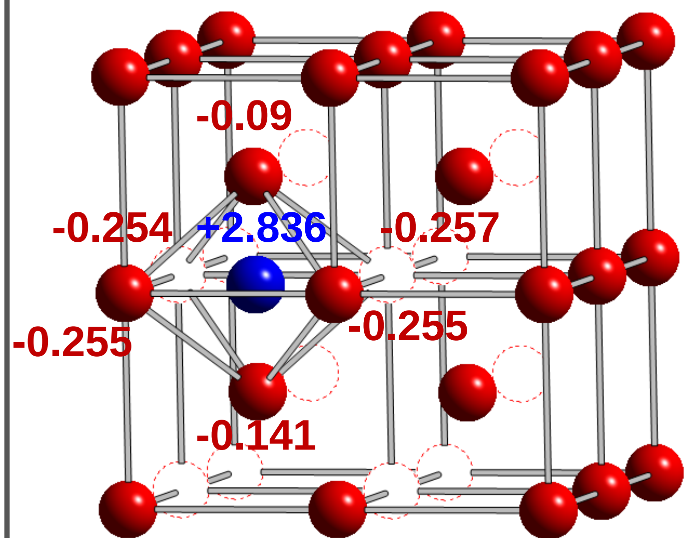
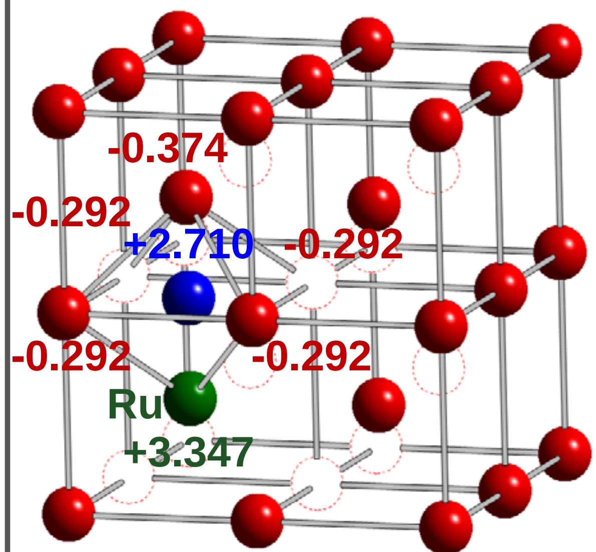
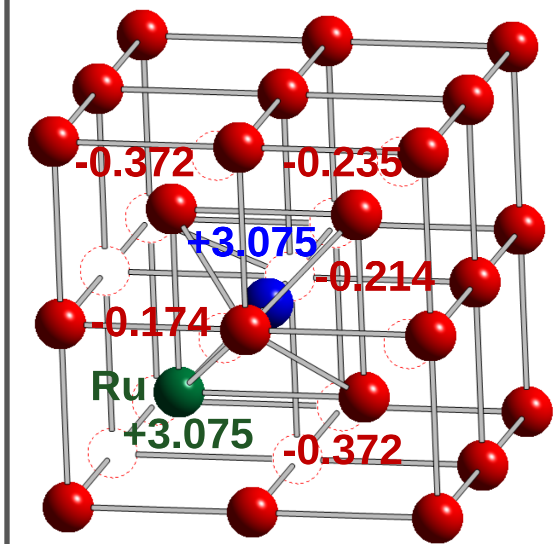
Density functional theory (DFT)

- Projector-augmented wave (PAW) potential
- GGA – PBE

Bulk vanadium	Lattice constant [Å]
This study	2.98
Previous calculation	2.93-2.94[1] 3.021[2]
Experiment	3.024[3]

[1]Mehl and Papaconstantopoulos, *Phys. Rev. B*, 1996; [2]Vitos et al., *J. Surf. Sci.* 1998; [3]Online CRC Handbook of Chemistry and Physics, 91[st] edition, 2010-2011

Increase Permeability by Alloying

Pure Vanadium	Distance (N-Ru)= 0.5 Å	Distance (N-Ru)= 0.71 Å
		
Lattice Constant= 3.01 Å E_b= -2.132 eV Lattice Expansion= 1.01%	Lattice Constant= 3.02 Å E_b= -0.889 eV Lattice Expansion= 1.34%	Lattice Constant= 3.01 Å E_b= -1.48 eV Lattice Expansion= 1.01%

H binding in V: O-site = -0.076eV; T-site = -0.280eV

Aboud and Wilcox, *J. Phys. Chem. C*, 2010;
Pauling-Scale Electronegativities: N = 3.04; V = 1.63; Ru = 2.2

Making Alloy-Based Membranes is Difficult!

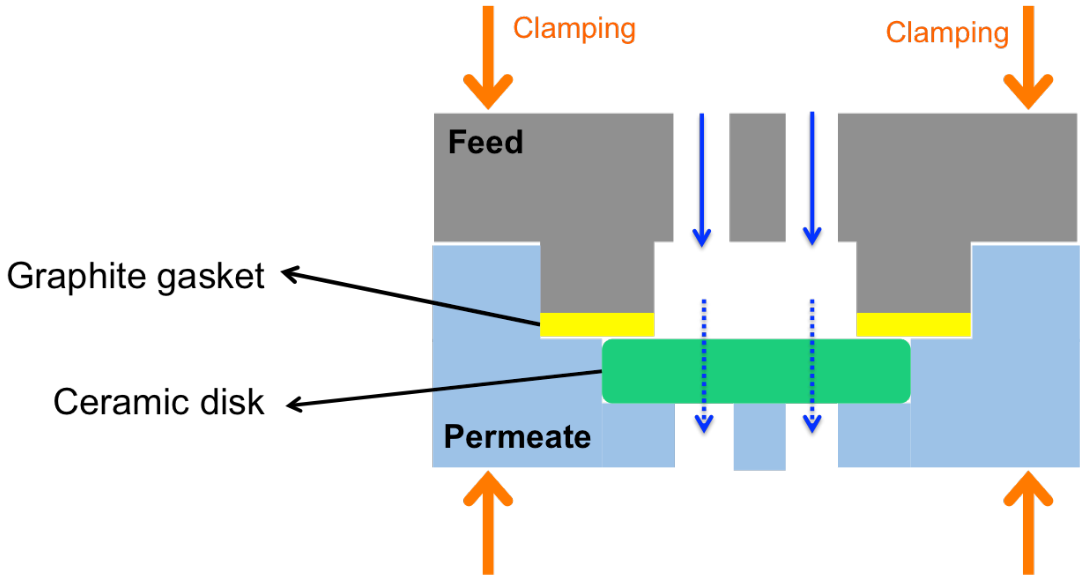
Alloy metal deposition strategy

Method	Characteristics	Availability
Sputtering	• Conformal and good adhesion • Slow (roughly 10-20 nm/min) • Limited thickness	Shared equipment at Stanford Nanofabrication Facility (SNF) Prof. William Chueh (Stanford) Dr. Steve Paglieri (TDA)
Evaporation	• Directional, moderate adhesion • Slow & limited thickness	Shared equipment at SNF and Stanford Nano Center (SNC)
Chemical Vapor Deposition (CVD)	• Metal oxide deposition (diffusion barrier) • Conformal & fast	Shared equipment at SNF

Shared facilities at Stanford for metal deposition

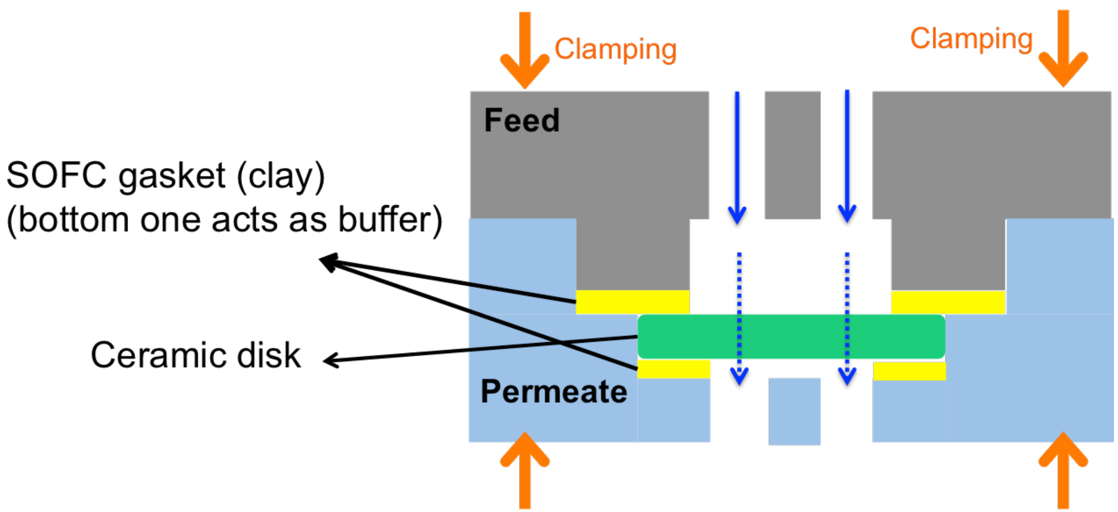
Name	Notes
KJ Lesker e-beam evaporator	Installed targets: Ti, Ta, Al, Au, Pd, Pt, Nb, and Ag. Additional materials possible based on user demand Thickness limited to couple of hundred nm Contact: Cliff Knollenberg (Spilker basement)
E-Beam Evaporator, Innotec	Installed targets: Ag, Al, Au, Co, Cr, Cu, Fe, Ge, In, Mo, Ni, Pd, Pt, Si, Ti, Ta, and W Allowed but not installed: Er, Hf, Ir, Ru, Tb, and Y Precious metal is limited to 200 nm; Others < 1µm
Magnetron sputtering, Metallica	Installed targets: Ag, Al, Au, Cr, Cu, Mo, NiCr, Pd, Pt, Ti, W and TiW 90/10wt% Rate: Au 60 nm/min, Ti, Cr 4 nm/min, Cu at 20 nm/min (one wafer at a time) Ferromagnetic materials (Co, Ni, Fe) cannot easily be sputtered. Max: 1µm (sputter should cool down after 10 min) Reasonably conformal film Maybe able to bring our own target (1” dia, 1/8” thick)

Improvements in membrane sealing in module



Previous

- One graphite gasket
- Temperature limited
- Ceramic breakage



Improvement

- Two SOFC gasket (made of clay)
- Higher operating temperature (>700˚C)
- Buffering ceramic disk

Consideration of Realistic Flue Gas

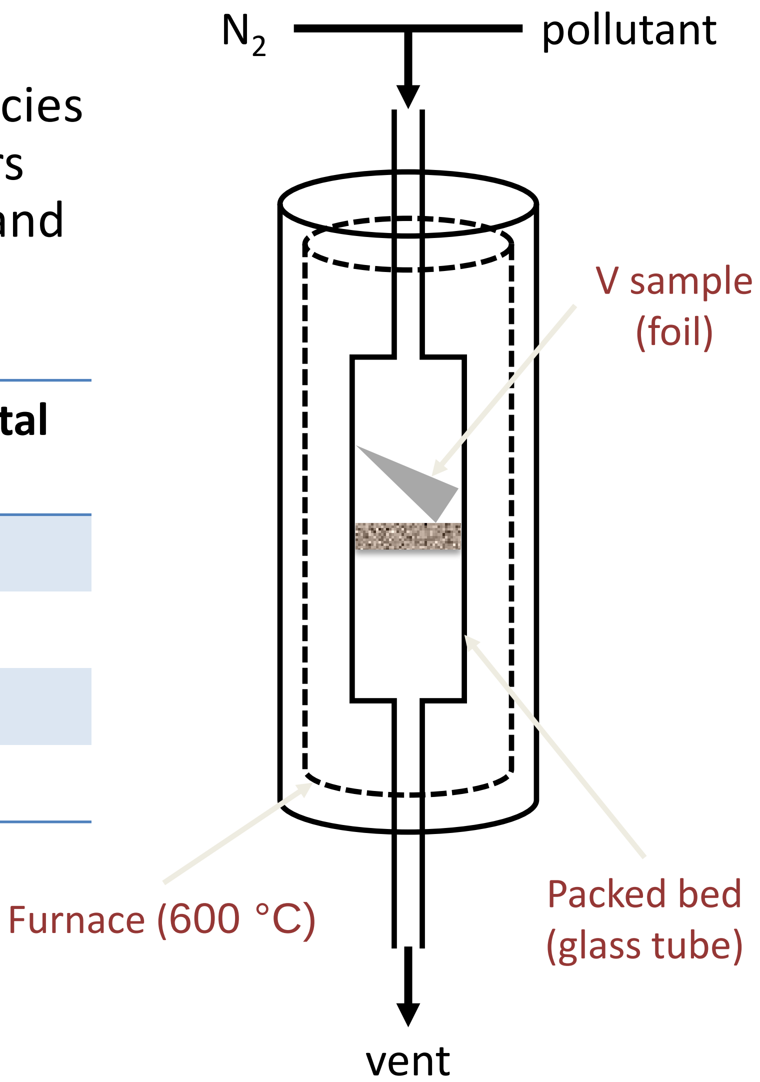
H_2O, NO, NO_2, SO_2

Experimental setup

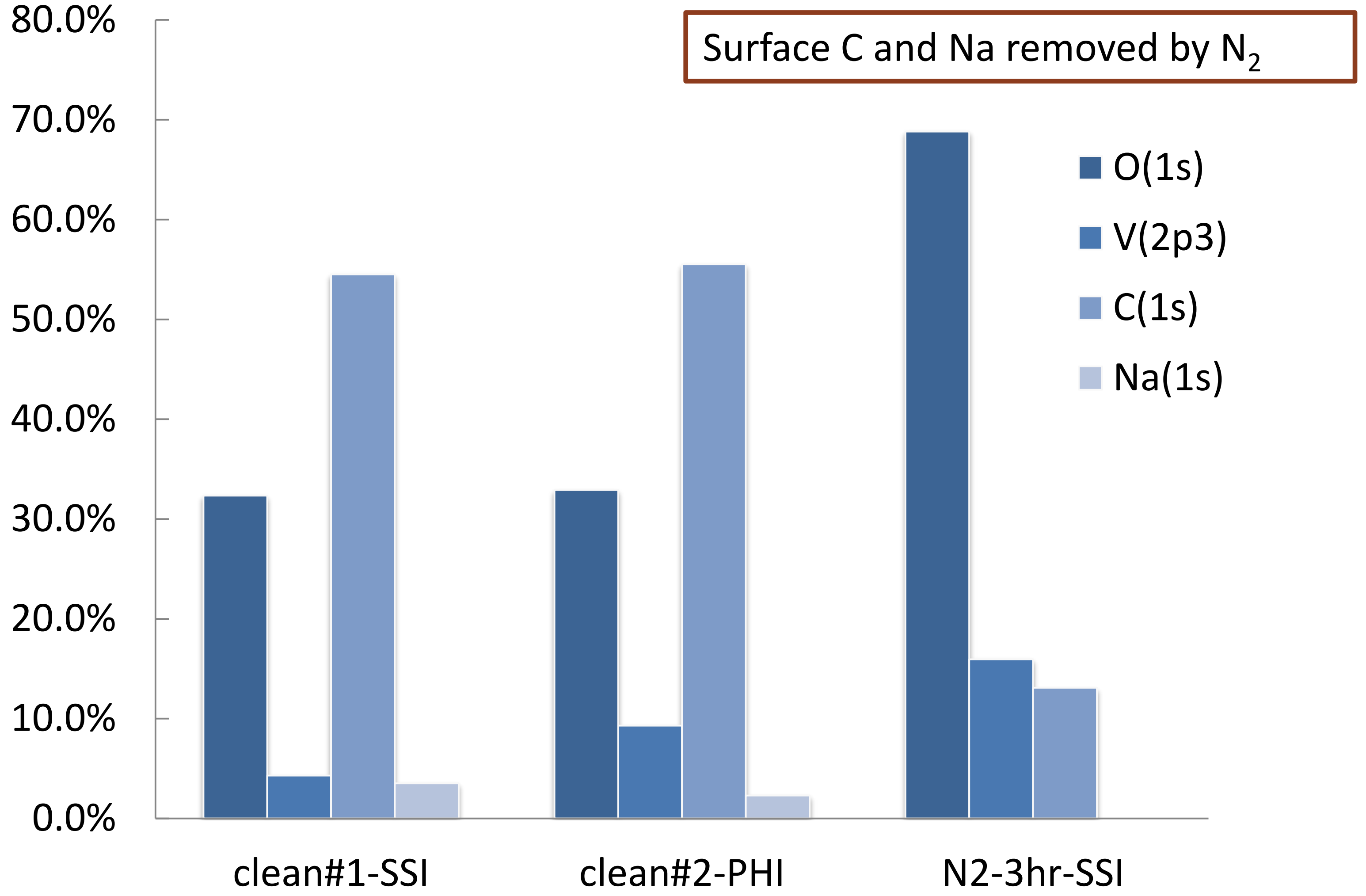
- Expose clean vanadium to each gas species (in N_2) at 600 °C for 1 hr, 3 hrs, and 5 hrs
- Follow up by XPS characterization (SSI and PHI)

component	reference flue gas* conc.	experimental conc.
H_2O(g) [vol%]	7.22%	10%
SO_2 [ppm]	425	495
NO [ppm]	231	245
NO_2 [ppm]	12	14

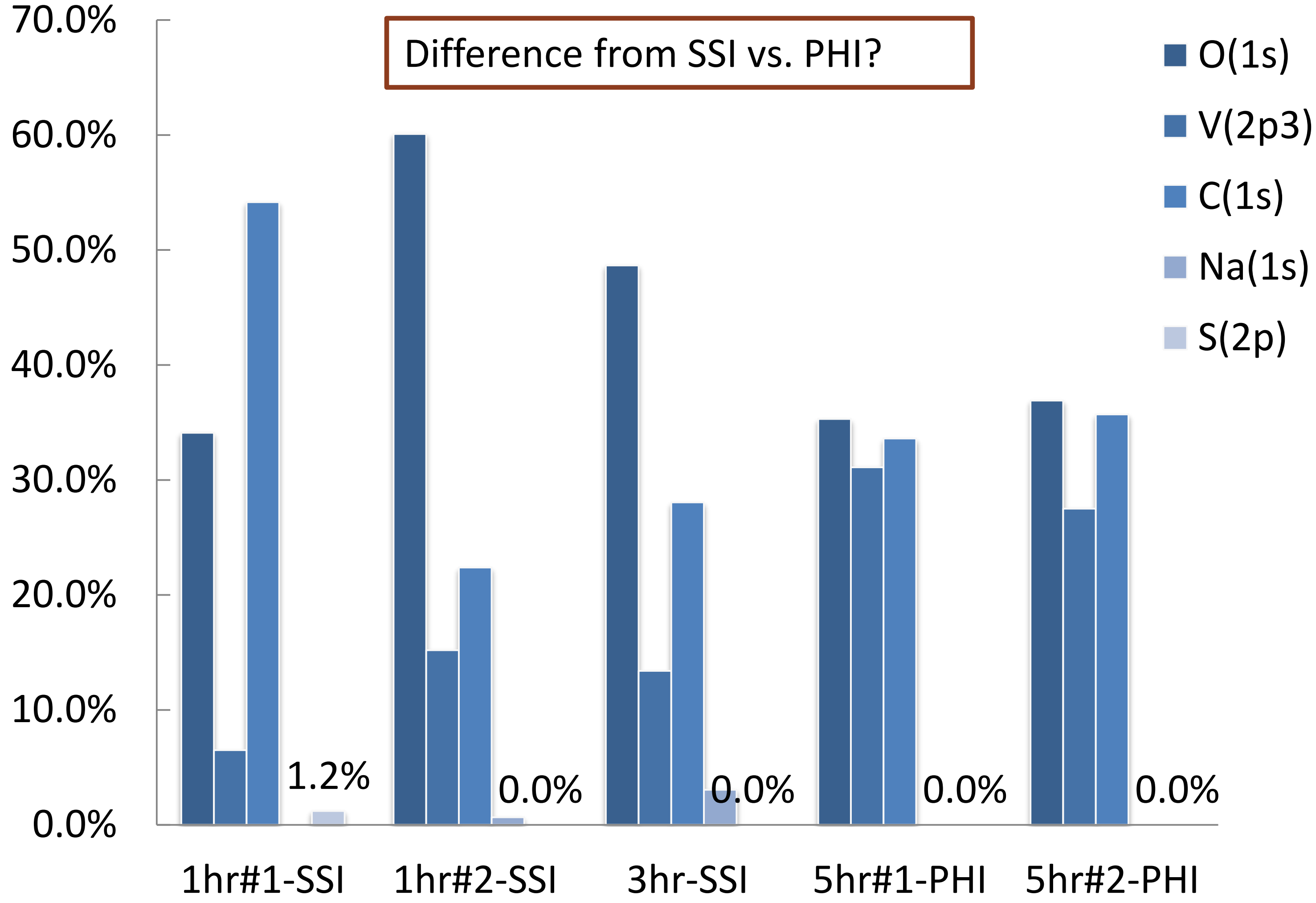
* coal: Appalachian Low Sulfur in IECM



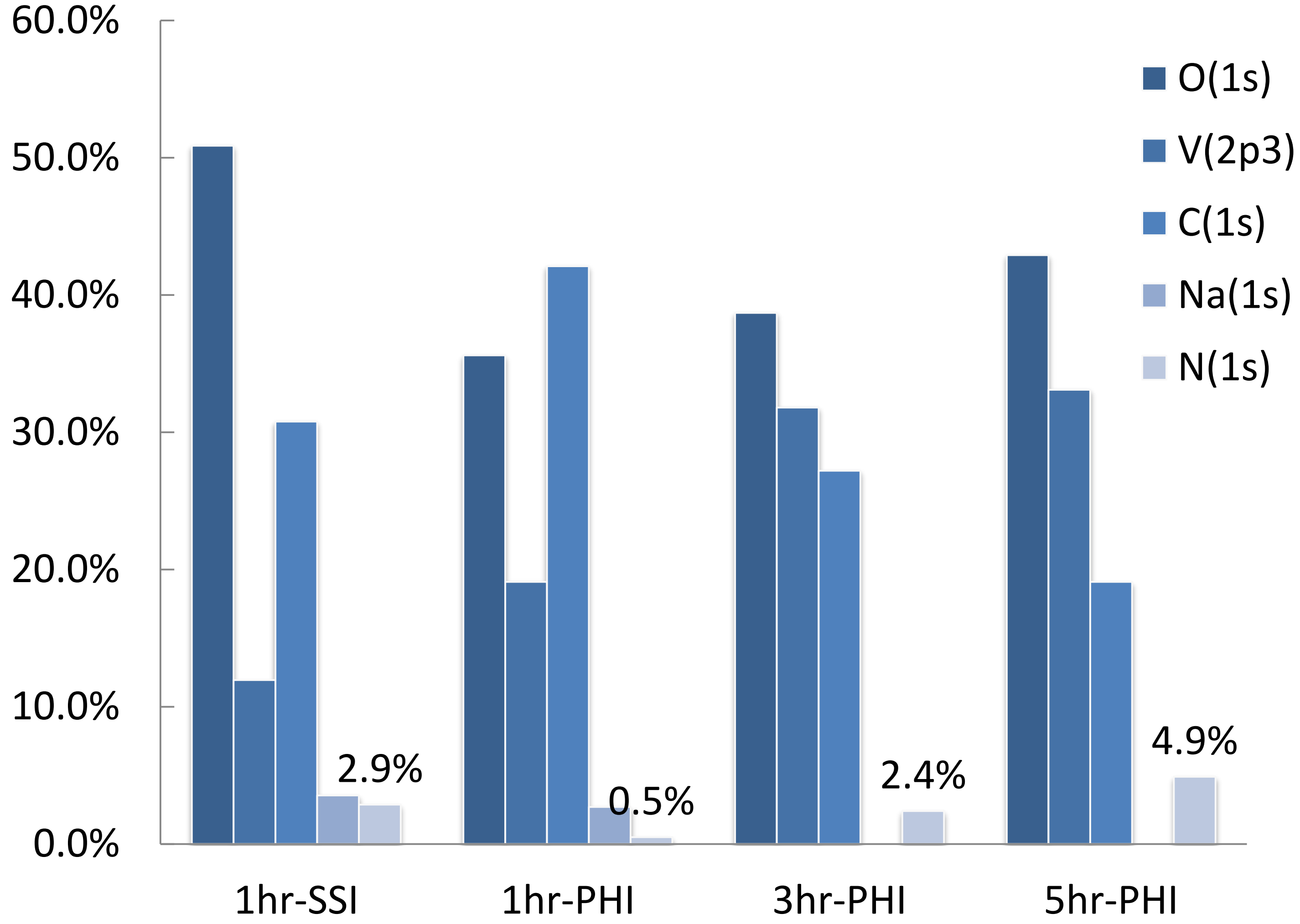
Blank V samples - unsputtered



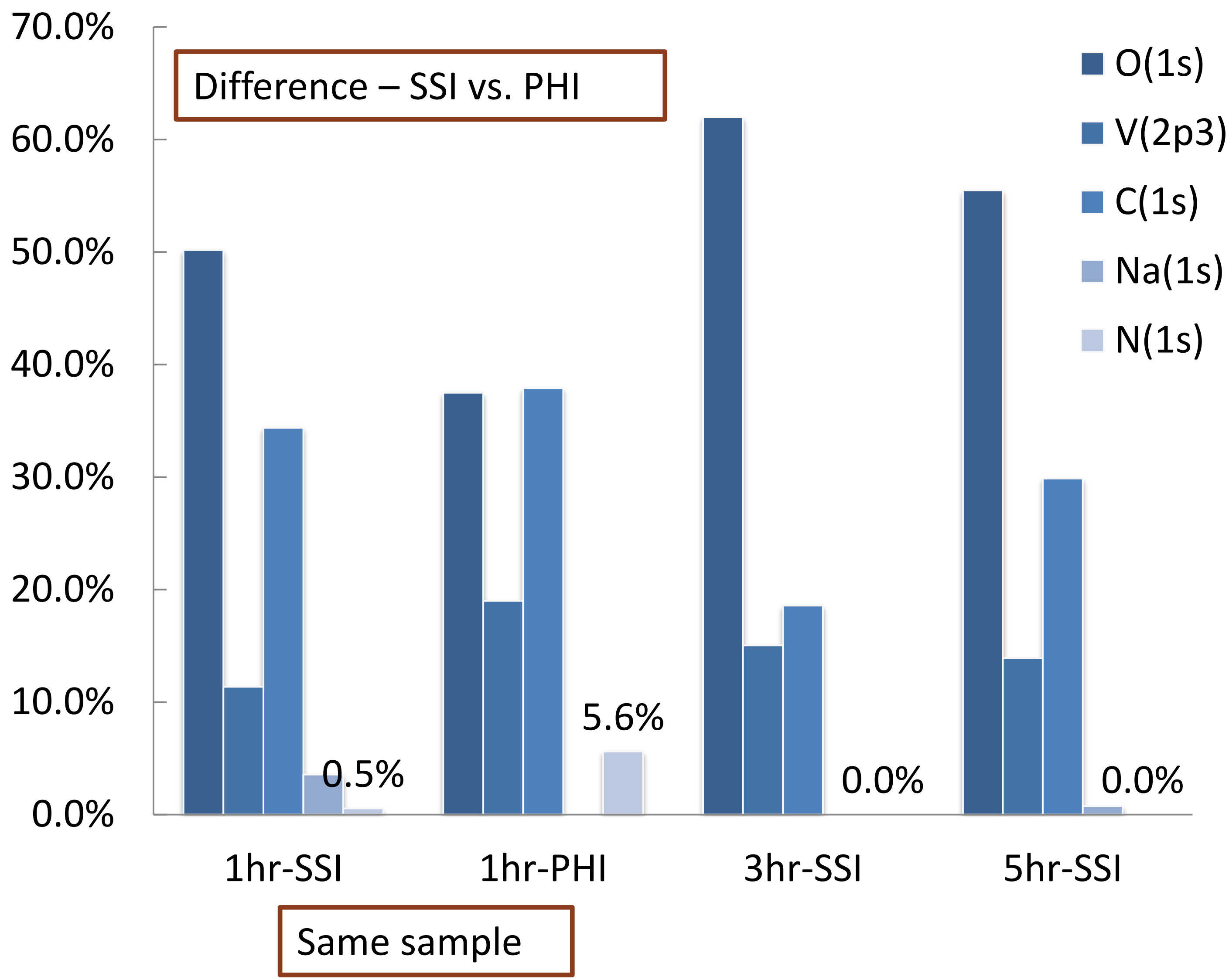
SO_2-exposed (495 ppm) V samples, unsputtered



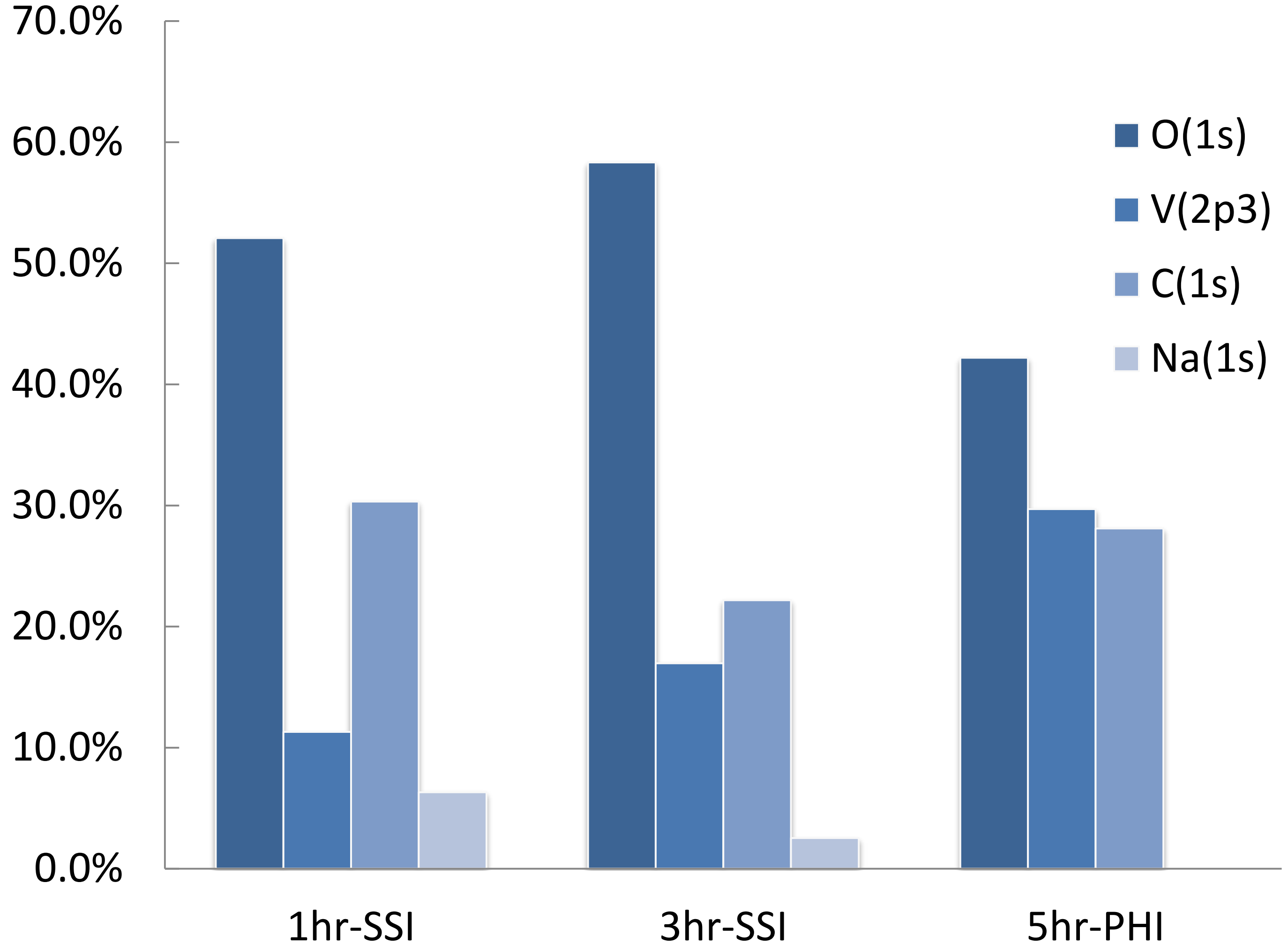
NO-exposed (245 ppm) V samples, unsputtered



NO_2-exposed (14 ppm) V samples, unsputtered



H_2O-exposed (10 vol%) V samples, unsputtered

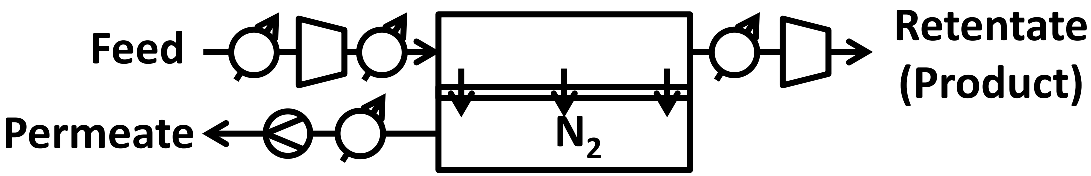


Where Does this Technology Fit Best?

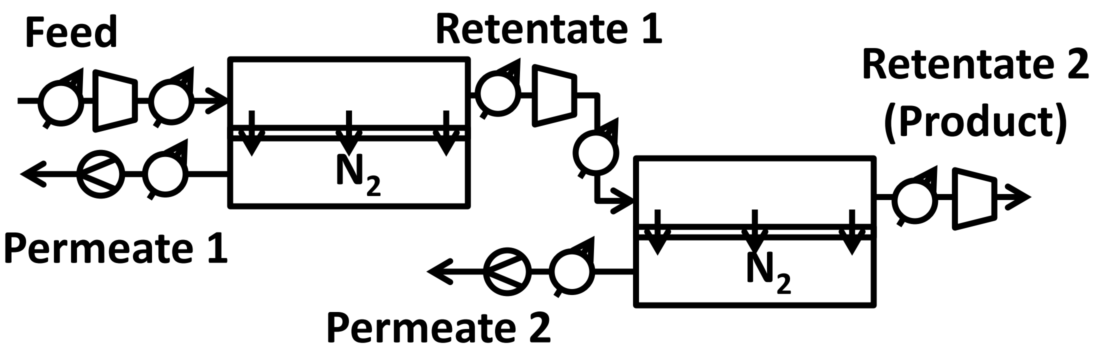
…in a power plant, ammonia synthesis

optimization helps to answer this

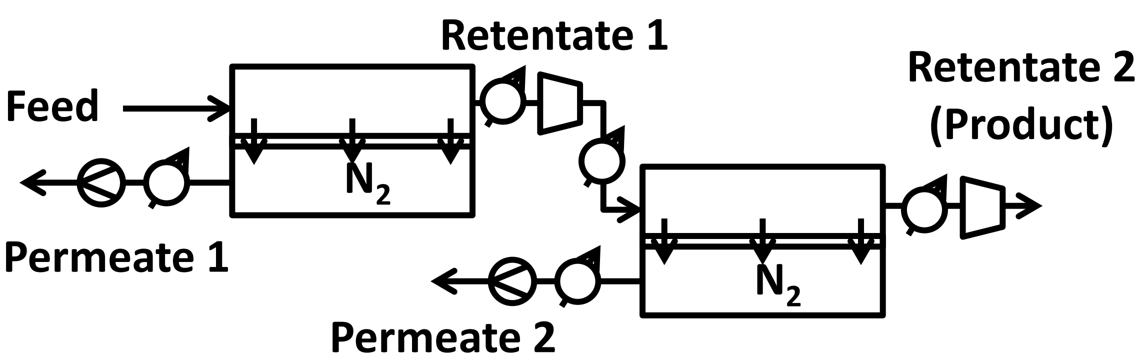
Membrane Configurations: N_2-Selective Membranes



Config. 1: Single-stage N_2-selective membrane



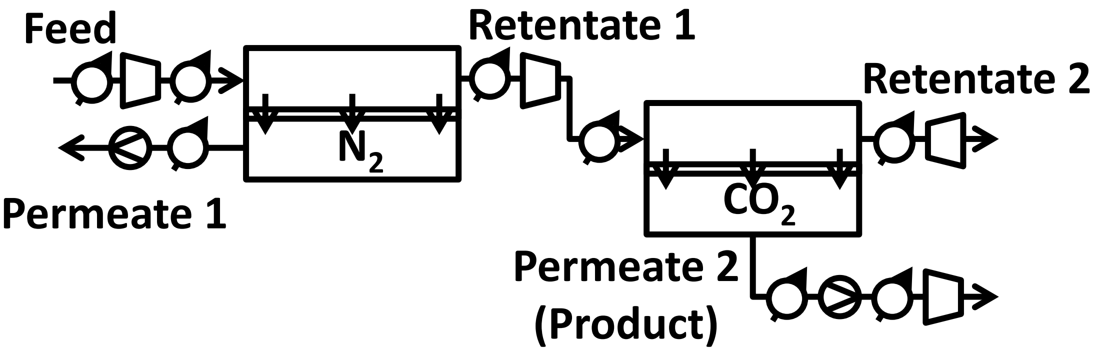
Config. 2: 2-stage N_2-selective membranes, with pressurization on 1st-stage feed



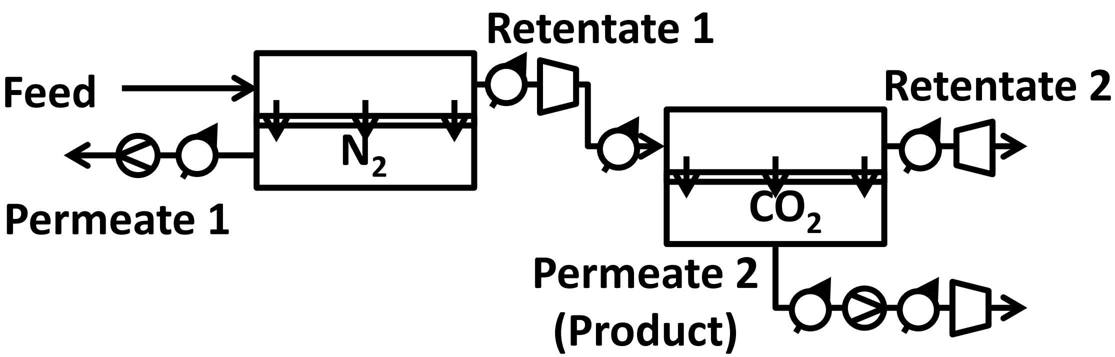
Config. 3: 2-stage N_2-selective membranes, **<u>no</u>** pressurization on 1st-stage feed

Muan, Wilcox, et al. *J. Mem. Sci.*, 2014

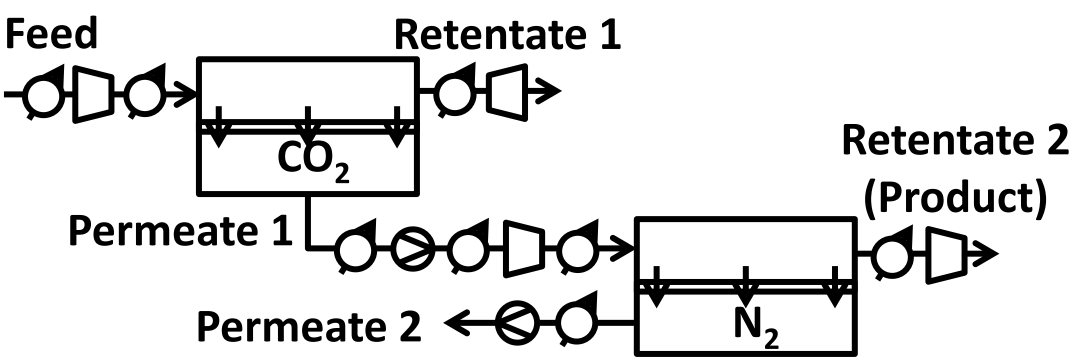
Hybrid Configurations: N_2- + CO_2-Selective Membranes



Config. 4: 1st-stage N_2-selective membrane with feed pressurization, 2nd-stage CO_2-selective membrane



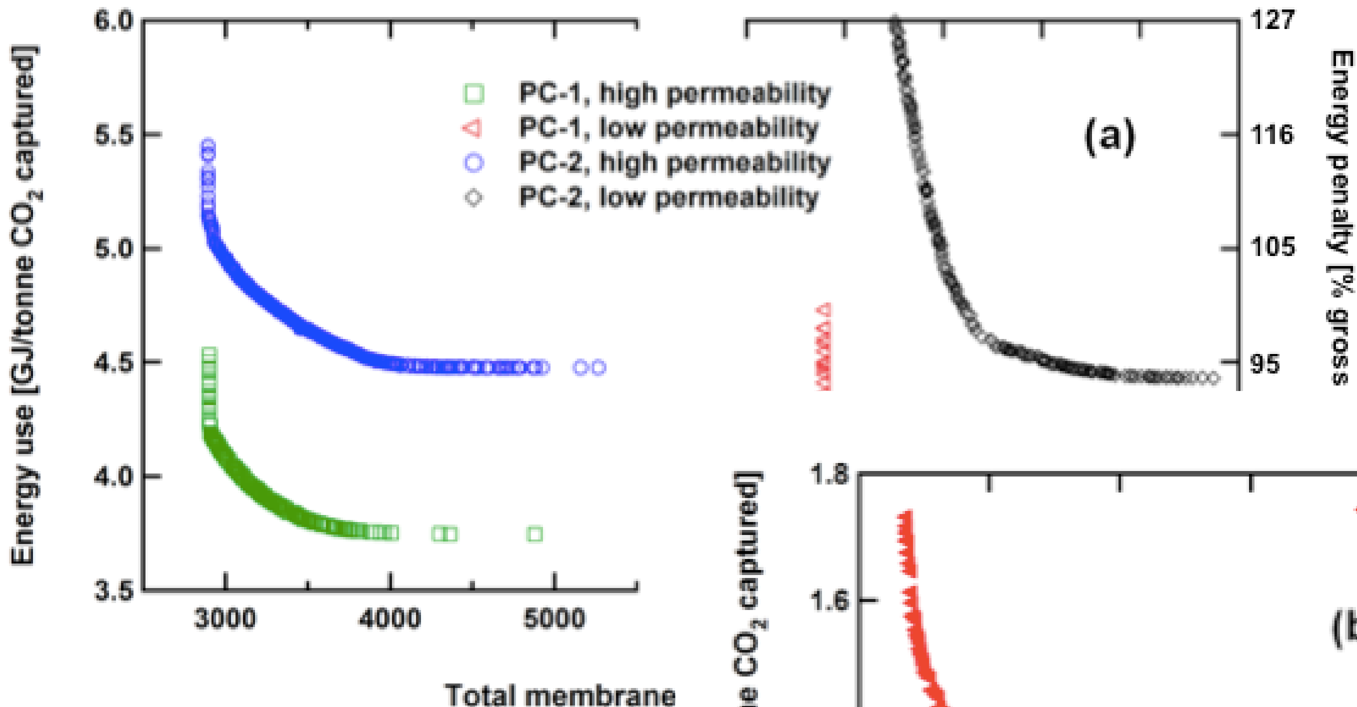
Config. 5: 1st-stage N_2-selective membrane with **no** feed pressurization, 2nd-stage CO_2-selective membrane



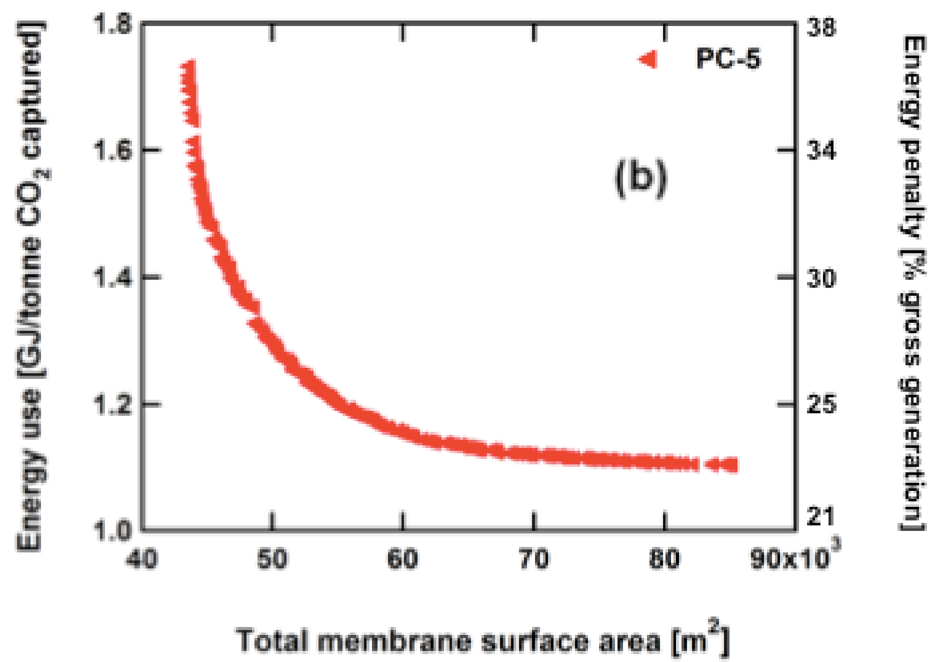
Config. 6: 1st-stage CO_2-selective membrane with feed pressurization, 2nd-stage N_2-selective membrane

Muan, Wilcox, et al. *J. Mem. Sci.*, 2014

Optimization Results



Promising Application
"CO_2 Enrichment"



Muan, Wilcox, et al. *J. Mem. Sci.*, 2014

In Summary

- Proof of Concept: nitrogen permeates through Group V metals and is selective over CO_2 via a solution-diffusion mechanism
- From DFT, atomic N draws significant charge from V leading to stabilization and “bonding” in the lattice
- Alloying with Ru significantly reduces atomic N stability in V
- Vanadium seems to be able to withstand acid gases, but further work is required
- N_2-selective membranes have shown great potential as **feed CO_2 enrichers** for CO_2-selective membranes
- Future work will involve investigation (ASPEN) of impact removal of N2 has on remainder of power plant operations
- Future work will include investigation of alloy synthesis and testing

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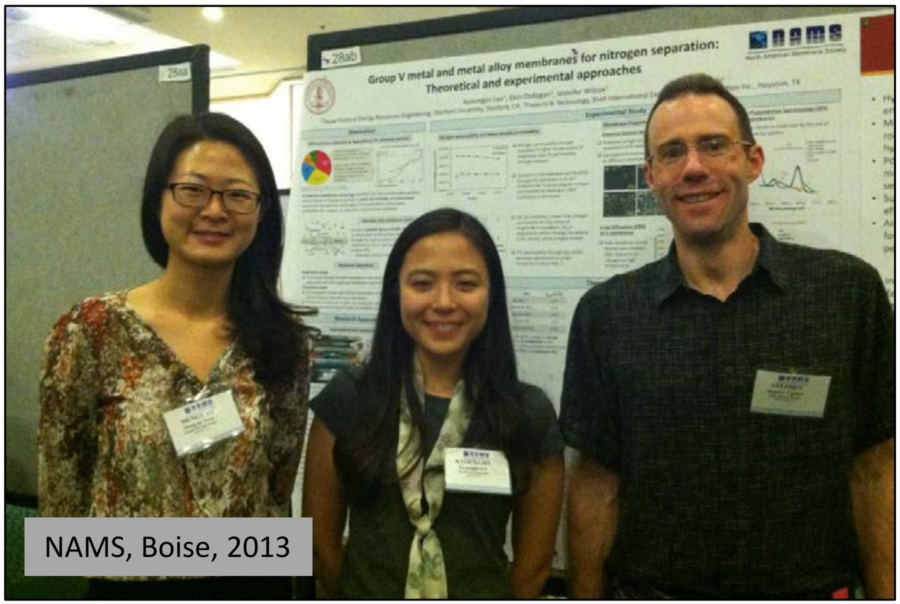
Dr Steve Paglieri, TDA Research



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- **Supercomputing:** CEES (Stanford), NSF Teragrid, UT Austin

Additional Information

Clean Energy Conversions Website: http://cec-lab.stanford.edu/

Questions?

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